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## APPLICATION OF NEODYMIUM OXIDE TO INCREASE THE WHITENESS OF PORCELAIN

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The spectral-colorimetric and luminescence characteristics of porcelain with neodymium oxide addition are studied. It is shown that whiteness increases when a small amount of neodymium oxide is present and that the coloring process begins as the neodymium oxide content increases. The increase in whiteness of porcelain is explained by a combination of two optical effects: increase of reflection in the blue-azure range of the visible spectrum due to sensitization radiation of the neodymium ion in the region 390 – 480 nm and a yellowness decrease due to the absorption of the neodymium ion in the interval 60 – 590 nm and a shift of the reflection peak into the blue-green region of the spectrum.

***Key words:*** porcelain, whiteness, color, neodymium oxide, kilning gas medium, luminescence.

One of the properties of porcelain is whiteness, which as a color property is determined by three independent variables: color value, hue, and saturation. Color value is evaluated on a white-black scale, while the combination of the hue and saturation determines the chromaticity. The lightness of porcelain depends predominately on the light scattering power (LSP) of the particles, which must have high LSP and relatively low absorption. The high whiteness of porcelain is also obtained with definite chromaticity — an azure hue with minimal saturation being preferable for users.

There exist several conventional methods of increasing the whiteness of porcelain [1]:

– increasing lightness by changing the hardening of porcelain, which can be controlled by means of the mineral composition, addition of mineralizers, mechanical activation, bioactivation of the initial components, and kilning time and temperature;

– decrease of saturation by decreasing the total content of the coloring iron and titanium oxides and changing the kilning conditions; as the soaking temperature or time at the maximum kilning temperature increases a system of color centers with low relative coloring power is formed.

In [2] the hypothesis that interfaces between glass and a crystalline phase affect light scattering in porcelain is confirmed on the basis of the theory of light propagation in strongly turbid media, especially in multiphase and polydisperse media such as porcelain.

There are two crystalline phases in porcelain — quartz and mullite, differing by the particle-size composition. Quartz grains are quite large, and the primary mullite particles are concentrated in the form of dense accumulations of lenticular shapes or aggregates larger than 30 – 50 μm, which is greater than the wavelength of visible light, so that light is predominately diffusely reflected from them. Particles of size 0.4 – 0.8 μm contain mainly crystals of secondary mullite, and then light scattering will be strongest and diffuse reflection from the surface greatest. As the kilning temperature and time increase, the volume fraction of the secondary mullite increases and that of primary mullite decreases. This correlation is attained at a lower kilning temperature of porcelain by introducing additions of mineralizers [3].

In [4] a classification of additives into four groups is proposed and the mechanism of their action is shown. Depending on their nature, amount, and composition the additives act in several stages. It has been shown that mineralizer additions change the color nature of porcelain. For example, additions of magnesium and calcium oxides increase the lightness and decrease the redness and yellowness of porce-

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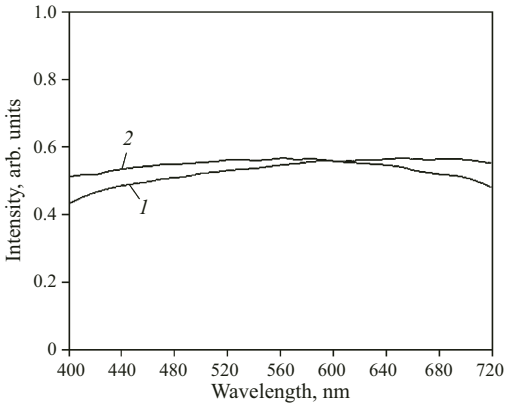


**Fig. 1.** Reflection spectra of porcelain samples kilned in different regimes: *1* ) in a medium-reducing gas (CO ≤ 2%) gas; *2* ) in a strongly reducing gas (CO ≤ 3.5%) gas.

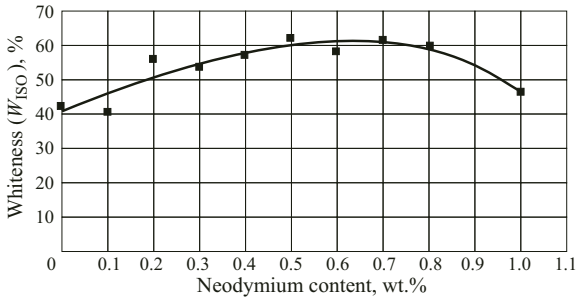


**Fig. 2.** Variation of the whiteness $W_{ISO}$ of porcelain versus the neodymium oxide content.

lain as a result of increasing the hardening of porcelain. When additives are introduced into the mix during kilning the volume fraction of the melt increases and the viscosity decreases, as a result of which the iron-containing complexes $Fe^{3+}$–O–$Fe^{3+}$ (clusters and associates) dissolve in it and become distributed over the volume of the melt in the form of [FeO] polyhedra, which greatly facilitates their reduction.

The main coloring impurities are iron and titanium oxides, which increase the color saturation and impart to porcelain red, yellow, or azure hues depending on the kilning conditions. According to [1] preferably white porcelains (high lightness with minimum saturation) can be obtained with coloring oxides content no more than 0.15 – 0.20%,[4] which is practically unattainable for the clayey raw materials used. Methods for whitening porcelain by introducing coloring additives, for example cobalt, are rarely used. A characteristic of this method of changing the hue of porcelain is that the reflection coefficient in the yellow-red region decreases, as a result of which reflection predominates in the blue-green region of the visible spectrum. Unfortunately, in this method of whitening porcelain the lightness decreases, which is perceived visually as an increase of the grayness on the white-black scale. The changes occurring in the color characteristics of porcelain as a function of the neodymium oxide content were analyzed in [5]. It was shown that as the content of additives increases the hue changes from yellow-green to blue-red, while the saturation with low content decreases practically to a minimum and increases with subsequent increase of the content.

The objective of this work was to study the effect of neodymium oxide addition to the porcelain composition and the kilning conditions on its spectro-colorimetric and luminescence characteristics.

The experimental samples were 50 × 50 mm porcelain plates made using the following initial materials (%): 35 – 45 kaolin, 5 – 10 clay, 20 – 30 quartz sand, and 20 – 30 pegmatite with neodymium oxide $Nd_2O_3$ added in amounts 0.1 – 1.0 with step 0.1%. The total $Fe_2O_3$ content in the porcelain composition was 0.3 – 0.4%.

The porcelain samples were prepared by slip casting and kilned in two different regimes:

1) maximum temperature 1350°C with CO content ≤ 2% in the gas medium (this kilning regime is used for porcelain decorated with subglaze cobalt paint, which is prone to reduction by carbon monoxide);

2) 1410°C and CO ≤ 3.5% (porcelain kilned without subglaze decoration).

The reflection spectrum of the samples was measured with two instruments:

– Pulsar spectrometer in which the sample is diffusely illuminated using an integrating sphere, equipped with a mirror trap under illumination/observation conditions D/8° with a *C* light source, reproducing the CIE standard radiation, and a 2° CIE 1931 standard observer in the wavelength range 380 – 720 nm;

– DC 3880 spectrometer (Data Color Company) in the wavelength range 400 – 700 nm with a CIE $D_{65}$ color source without and with a UV cut-off filter; compared with the *C* light source the $D_{65}$ source has a high UV content, so that the measurement was performed by two methods — neglecting and taking account of the UV component.

If a beam of white light, for example, from light source *C*, strikes the surface of a sample of white porcelain, then light mirror or diffusely reflected from the surface as well as partially absorbed will be white with a hue. The mirror reflected light will increase the lightness of the samples, while the samples will be visually perceived as whiter. Because the mirror component of the reflected light depends on the state of the surface this component of the light was excluded when measuring the reflection spectrum [6].

The basic terms and indices used for the color characteristics when analyzing the concentration dependences of the neodymium oxide content in porcelain are as follows [7]:

– color – lightness coordinates $L^*$ and chromaticity: from green ($-a^*$) to red ($+a^*$) and from blue ($-b^*$) to yellow ($+b^*$) in the CIE metric system $L^*a^*b^*$ 1976;

– dominant wavelength $\lambda_d$ in the CIE 1931 metric system;

[4] Here and below, content by weight.

**TABLE 1.** Color Characteristics of Porcelain Samples

| Kilning regime | Color coordinates | | | Whiteness $W_{ISO}$, % | Dominant wavelength, nm |
|---|---|---|---|---|---|
| | $L^*$ | $a^*$ | $b^*$ | | |
| First | 79.80 | –0.31 | 5.13 | 38.88 | 576.1 |
| Second | 80.57 | –1.54 | 1.88 | 47.75 | 564.7 |

– whiteness $W_{ISO}$ according to the ISO 105-J02 standard.

An instrumental-methodological system was used to study the spectral-kinetic characteristics of the luminescence of the samples [8]. The luminescence spectrum was measured with and without a delay of 180 μsec after the laser pulse in molecular nitrogen ($\lambda_{meas}$ = 337.1 nm) in the wavelength range 380 – 850 nm.

Increasing the temperature and changing the composition from weakly to strongly reducing during kilning of the porcelain increases whiteness; this is confirmed by the data in Table 1. Comparing according to the color characteristics two batches of porcelain samples with identical initial mineral and chemical compositions but kilned in different regimes reveals the following changes: increase of whiteness $W_{ISO}$ by 9% (from 38.9 to 47.9%); substantial decrease of the yellowness values along the coordinate $b^*$ (yellow-blue) from 5.13 to 1.88 and, to a lesser degree, the redness along the coordinate $a^*$ (red-green) from – 0.31 to – 1.54, respectively. In consequence, as the values along the chromaticity coordinates decrease, color saturation decreases and, correspondingly, the whiteness of porcelain increases. The increase in lightness $L^*$ is very small (from 79.8 to 80.6) and contributes a small amount to the increase of the whiteness of porcelain.

The decrease of the yellowness of porcelain after kilning in a strongly reducing gas medium is due to the transition Fe(III) → Fe(II), which is confirmed by the reflection spectrum (Fig. 1). A decrease of the reflection coefficients toward the UV region of the spectrum is observed in curve *1*, corresponding to the reflection spectrum of samples kilned in a weakly reducing gas medium; this decrease is explained in [9] by a strong absorption band $O^{2-} \rightarrow Fe^{3+}$ in the UV region of the spectrum in the wavelength range 230 – 320 nm, whose long-wavelength edge catches the optical region of the spectrum.

Conversely, a decrease of the reflection coefficient in the direction of the IR region of the spectrum is seen in curve *2*, corresponding to the reflection spectrum of samples kilned in a strongly reducing gas medium. This decrease is explained by a strong absorption band $O^{2-} \rightarrow Fe^{3+}$ in the near-IR region of the spectrum [9], whose short-wavelength edge catches the optical region of the spectrum.

Thus, in the first place, a change of the composition of the gas medium from weakly to strongly reducing during kilning of porcelain with iron oxides content > 0.3% does not permit reaching high values of whiteness $W_{ISO}$; in the second place, the particulars of the production of artistic porcelain decorated with subglaze cobalt paint are such that there are limits on the maximum kilning temperature (≤ 1340°C) as well as on the oxidation-reduction potential of the gas medium in the atmosphere of the kiln. At higher temperatures with a reducing gas medium cobalt oxide is reduced to the metal state, which lowers the quality of the porcelain articles, so that the main objects of study were porcelain samples with $Fe_2O_3$ content > 0.3%. The effect of neodymium oxide on the whiteness of porcelain kilned at 1340°C in a chamber furnace with a weakly reducing gas medium can be judge from the spectro-colorimetric and luminescence properties of the porcelain samples.

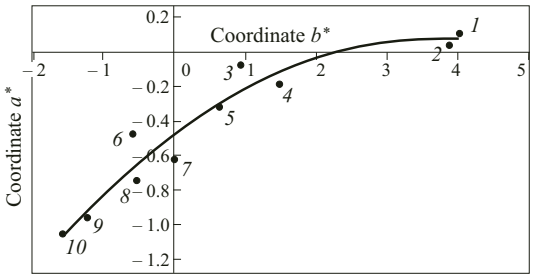


**Fig. 3.** Variation of the chromaticity coordinates $a^*$ and $b^*$ in the CIE 1976 system $L^*a^*b^*$ of porcelain samples versus the neodymium oxide content (wt.%): *1* ) no additives; *2* ) 0.1%; *3 – 9* ) 0.2 – 0.8%; *10* ) 1.0%.

Analysis of the values of the whiteness $W_{ISO}$ of porcelain as a function of its $Nd_2O_3$ content in comparison with the corresponding values of the lightness coordinate $L^*$ and the chromaticity coordinates $a^*$, $b^*$ of porcelain samples with no additives showed the following:

– as the $Nd_2O_3$ content increases from 0.2 to 0.8% the whiteness $W_{ISO}$ increases by 11.5 – 19.5% while for content > 0.8% whiteness decreases to 48% (Fig. 2);

– for $Nd_2O_3$ content from 0.2 to 0.4% mainly the yellowness $b^*$ decreases (from 4.0 to 0.8) with decreasing saturation and for $Nd_2O_3$ content > 0.6% yellowness $b^*$ and redness $a^*$ decrease as the hue changes from yellow-green to blue-green with increasing saturation (Fig. 3).

Therefore, depending on the $Nd_2O_3$ content, equal to 0.2 – 1.0%, two optical effects are observed in the porcelain composition: from 0.2 to 0.6% — increase in whiteness and for > 0.6% — coloring of porcelain with increasing lightness and change of hue predominate.

The ratio $J_0$ of the reflection coefficient of porcelain samples with $Nd_2O_3$ to the corresponding reflection coefficient of porcelain with no additives was calculated as a function of the wavelength (Fig. 4). Three wide peaks are observed in the curve of the relative reflection coefficient of the porcelain with $Nd_2O_3$ addition: the first peak corresponds to an increase of the reflection in the blue-azure region and the second and third peaks correspond to a decrease of the reflection in the green-yellow region, which result in a change of the visually perceived hue of white porcelain from yellow

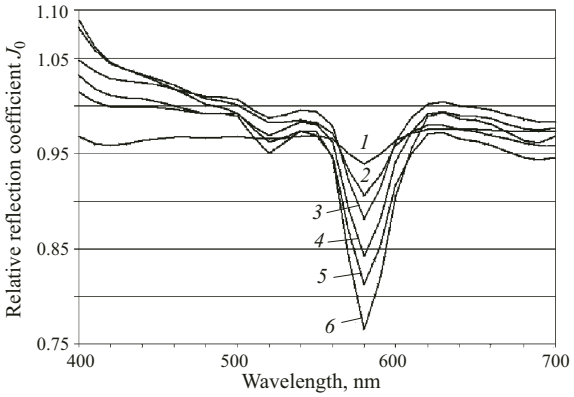


**Fig. 4.** Variation of the relative reflection coefficient $J_0$ of the porcelain samples versus the neodymium oxide content: *1* ) 0.1%; *2* ) 0.2%; *3* ) 0.3%; *4* ) 0.4%; *5* ) 0.5%; *6* ) 0.6%.

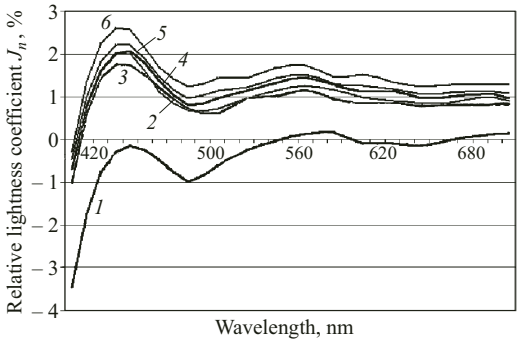


**Fig. 5.** Variation of the relative reflection coefficient $J_n$ of the porcelain samples versus the neodymium oxide content: *1* ) 0.1%; *2* ) 0.2%; *3* ) 0.3%; *4* ) 0.4%; *5* ) 0.5%; *6* ) 0.6%.

to azure. It was shown that the values of $J_0$ are positive for porcelain samples with $Nd_2O_3$ content 0.2 – 0.6% for wavelengths in the interval 400 to 480 nm corresponding to the blue-azure region of the visible spectrum. Samples with 0.2 – 0.3% $Nd_2O_3$ have the highest values of $J_0$.

The two peaks in the intervals 500 – 540 and 560 – 620 nm with the lowest values of the relative reflection coefficient $J_0$ for porcelain samples [5] with different $Nd_2O_3$ content (see Fig. 4) are similar to the peaks in the absorption spectrum of neodymium [10].

It is known [7] that if white samples differ by their azure color (decrease of yellowness $b^*$), then the whitest samples have the stronger azure color. Depending on the balance of the brightness and azureness porcelain samples will be perceived as whiter or more azure in color. In addition, for $Nd_2O_3$ content 0.2 – 0.4% the brightness shows practically no decrease, which uncharacteristic when coloring additives are introduced, even if their coloration power is low [5].

It has been proposed that neodymium in porcelain absorbs energy in the near-UV region and emits energy in the visible region in a wide, weak band of luminescence radiation. When a UV-cutoff filter is used, the luminescence can be completely eliminated and the reflection coefficient can be measured in the absence of luminescence. The reflection coefficient curves obtained in both measurement regimes are identical for nonluminescing and different for luminescing porcelain samples.

Because the spectral curve of luminescing samples represents simultaneously reflected light and luminescence radiation it would be inaccurate to call it a spectral reflection curve. For this reason, such curves are called spectral lightness curves [7]:

$$\beta_t = \beta_\gamma + \beta_f,$$

where $\beta_t$ is the lightness coefficient, $\beta_\gamma$ is the reflection coefficient, and $\beta_f$ is the lightness coefficient due to luminescence.

To determine the luminescence fraction in the visible region of the reflection spectrum of porcelain samples containing neodymium oxide the relative lightness coefficient $J_n$ is introduced:

$$J_n = \frac{J_2 - J_1}{J_1} \times 100\%,$$

where $J_1$ is the reflection coefficient of porcelain measured without the UV component in the spectrum of the light source and $J_2$ is the reflection coefficient of porcelain measured with the UV component in the spectrum of the light source.

The relative lightness coefficient $J_n$ of a porcelain sample with 0.1% $Nd_2O_3$ is negative in practically the entire interval of the visible spectrum. This effect is explained by the superposition of the absorption bands $O^{2-} \rightarrow Fe^{3+}$ and $Nd^{3+}$ in the UV region of the spectrum, where the long-wavelength edge of the bands catches the visible region of the spectrum (Fig. 5). As the $Nd_2O_3$ content in the porcelain increases from 0.2 to 0.6% the relative lightness coefficient $J_n$ is positive in a wide band of the visible spectrum peaking in the region 415 – 480 nm.

Therefore, a whitening luminescing additive increases the lightness coefficient over the entire visible spectrum, and especially in the violet-blue region. This optical effect can be explain the contradictory data which were presented previously: the reflection spectrum of porcelain with $Nd_2O_3$ added has intense peaks with a minimum of the reflection coefficient in the regions 500 – 540 and 560 – 620 nm, which should decrease the lightness but, as follows from the values of the colorimetric characteristics, the lightness of porcelain with 0.2 – 0.3% $Nd_2O_3$ does not decrease with increasing azureness (see Fig. 4).

The source of luminescence in porcelain was determined from the luminescence spectrum. The spectra were obtained with and without a delay of 180 μsec after the laser pulse. The high sensitivity of the method [8] made it possible to detect the luminescence band of uranyl $(UO_2)^{2+}$ and $Fe^{3+}$ (Fig. 6) in porcelains with and without neodymium oxide ad-

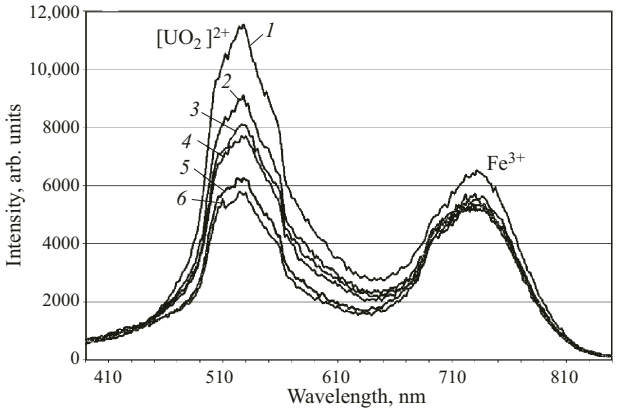


**Fig. 6.** Variation of the intensity of the luminescence bands of uranyl $(UO_2)^{2+}$ and $Fe^{3+}$ versus the neodymium oxide content in porcelain: *1* ) no neodymium oxide addition; *2* ) 0.1%; *3* ) 0.2%; *4* ) 0.3%; *5* ) 0.4%; *6* ) 0.5%.

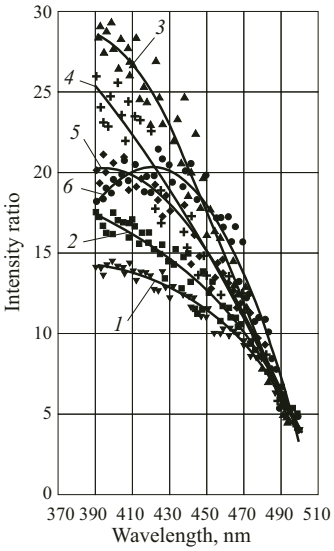


**Fig. 7.** Variation of the ratio of the intensity of the band in the luminescence spectrum of porcelain samples measured without a delay versus the neodymium content to the intensity of the corresponding band measured with a delay of 180 μsec after the laser pulse. Neodymium oxide content: *1* ) no neodymium oxide addition; *2* ) 0.1%; *3* ) 0.2%; *4* ) 0.3%; *5* ) 0.4%; *6* ) 0.5%.

dition. The presence of uranyl in porcelain is explained by its presence in small quantities in sedimentary rocks. Uranyl is a strong luminophor even at content below the MAC.

As $Nd_2O_3$ content increases from 0.1 to 0.6% the intensity of the uranyl $(UO_2)^{2+}$ band in the luminescence spectrum decreases (Fig. 6), while the $Fe^{3+}$ band intensity changes very little.

The most informative indicator characterizing the changes in the luminescence properties of porcelain with $Nd_2O_3$ addition is the ratio of the intensity of the band in the luminescence spectrum measured without a delay to the corresponding band measured with a delay equal to 180 μsec after the laser pulse (Fig. 7).

It was determined that 0.2 – 0.6% $Nd_2O_3$ in porcelain increases the intensity ratio of the luminescence band in the 390 – 500 nm, which attests to weaker decay of the luminescence. The ratio of the luminescence bands reaches its maximum value with 0.2% neodymium oxide added, and as the neodymium content increases the luminescence intensity ratio decreases.

It is well known [11] that in a number of solid solutions the uranyl ions $(UO_2)^{2+}$ (donor) give up their excitation energy (sensitization process) to the $Nd^{3+}$ ions (acceptor). The energy transfer process proceeds by means of nonradiative transfers of electronic excitation energy [12]. This supposition is supported by the ratio of the band intensities in the luminescence spectrum of porcelain samples with different neodymium oxide content (see Fig. 7). The luminescence photon yield is proportional to number of complexes in which $(UO_2)^{2+} – Nd^{3+}$ excitation energy transfer is followed by luminescence of neodymium ions. To create such complexes in porcelain it is sufficient to introduce 0.2 – 0.5% neodymium oxide. Large amounts are not desirable because the relative reflection coefficient close to the UV region would decrease as a result of concentration quenching of the luminescence.

In summary, the mechanism of the increase of the whiteness of porcelain with neodymium oxide additions can be understood on the basis of theoretical and experimental studies. The addition of neodymium oxide to porcelain increases the perceived whiteness because of a combination of diffuse reflection from the surface and secondary radiation in the form of light. The whiteness of porcelain increases with a small amount of neodymium oxide in a definite interval; the coloring process starts at higher content. The values of the colorimetric indices are available for 0.2 – 0.8% neodymium oxide in porcelain: saturation decreases with a change hue from yellow to azure, which user's prefer, with stable lightness of the porcelain.

The increase of the whiteness of porcelain is explained by a combination of two optical effects: the first one is an increase of the reflection in the blue-azure region of the visible spectrum due to sensitized optical-range luminescence of the neodymium ion in the form of a wide weak band; the second one is a decrease of the reflection in the yellow-green region due to the absorption of the neodymium ion in the intervals 500 – 540 and 560 – 620 nm. In aggregate this makes it possible for reflection to dominate in the blue-green region of the spectrum.

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